

# **Review of the Updated Maximum Incremental Reactivity Scale of Dr. William Carter**

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## Abstract

The purpose of this report is to provide the California Air Resources Board with a peer review of Dr. William P.L. Carter's detailed chemical mechanism. Carter's mechanism is being proposed as a basis for VOC control regulations based on reactivity calculations. We have performed a peer review of Carter's detailed chemical mechanism, its documentation and supporting databases. The chemical kinetic data in the mechanism and its supporting material were compared with data from standard kinetic databases, such as DeMore et al. (1997), Atkinson et al. (1997) and Atkinson (1994) and the most recent available literature. The kinetic parameters checked included the reactions, rate constants, product yields and lumping methods. Finally all documentation was reviewed to ensure that the mechanism, all supporting documents and all computer codes are clearly described. The objective of our peer review was to ensure that the Carter's detailed mechanism consists of the best possible atmospheric chemistry that is now available and that it is well documented.

Dr. Carter is to be commended for developing a high quality mechanism that is state of the science for air quality modeling. The mechanism is clearly within the realm of the best available science. Air quality models that make use of previous versions of Dr. Carter's mechanism should update to this new version. But the rate parameters of the mechanism should include correct temperature and pressure dependencies rather than any "fits" for surface temperature and pressure. Although the simplified expressions might be adequate for reactivity calculations, they are not acceptable if the mechanism is to be implemented in regional scale air quality models such as EPA's Models3.

The mechanism makes full use of the available kinetic data and reflects the considerable progress that has been made in improving our understanding of atmospheric chemistry. However there remain several important outstanding issues to be resolved by further experimental studies including: better mechanistic data for most higher molecular weight organic compounds; more data on the product yields for the reactions of HO, NO<sub>3</sub> and O<sub>3</sub> with alkenes; and fundamental data on aromatic reaction mechanisms.

Carter's scheme of assigning organic compounds to 11 bins based on the compound's mechanistic uncertainty is reasonable. The assignments made by him appear to be reasonable in view of the current state of chemical knowledge.

A minimum multiplier of 1.5 should be used to estimate the uncertainty in all MIRs. This is based on the range of the average coefficient of variation being between 0.28 and 0.41 and on the fact that the MIRs increased between 1994 and 1998 by 47%. It would seem reasonable based on the past changes to assume that any MIR might vary by 50% in future calculations. Bins 1 to 4 should be adjusted by a factor of 1.5. Based on this analysis a factor of 2 is a large enough adjustment for bin 5 and higher bins. It is suggested that these new factors are a more reasonable method of handling uncertainty in MIRs while minimizing the possibility of underestimating a product's reactivity. Use of these proposed higher factors is a reasonable method of handling uncertainty in MIRs while minimizing the possibility of underestimating a product's reactivity.



# 1. Introduction

The California Air Resources Board (CARB) is considering development of volatile organic compound (VOC) control regulations for aerosol coatings based on the maximum incremental reactivity scale (MIR) (Carter, 1994). Regulations based on ozone formation potentials (reactivity) may provide a more cost-effective alternative to purely mass based regulations. The MIRs to be used within this program are based on calculations made with Carter's updated chemical mechanism. Because the detailed updated mechanism consists of hundreds of parameters it must be carefully peer reviewed to be credible.

VOC control strategies aimed at reducing the photochemical formation of ozone have been primarily based on reducing the mass of VOC emitted regardless of the chemical nature of the VOC. However, it is well known that VOCs are oxidized in the atmosphere through very different mechanisms. For example, alkanes and aromatics react only with hydroxyl radicals (HO) in the gas-phase while alkenes react with HO, ozone and nitrate radical (NO<sub>3</sub>) (Atkinson, 1994). Oxygenated compounds such as formaldehyde (HCHO) also photolyze to produce radicals in addition to reacting with HO and NO<sub>3</sub> (Atkinson, 1994).

The contribution of each VOC to the formation of ozone is different because each has a different oxidation mechanism in the atmosphere. The ozone formation potential has been characterized by several different measures but the MIR scale (Carter, 1994) is widely used and it has been investigated for potential applications through a number of investigations (Russell et al., 1995; Yang et al. 1995; 1996; Stockwell and Kuhn, 1998).

For a specified scenario of meteorological conditions, emissions and initial concentrations, an incremental reactivity, IR, of an organic compound is the change in the peak ozone concentration, [O<sub>3</sub>] in grams, divided by an incremental change in the initial concentration and emissions of the organic compound, [VOC] in grams, (Carter, 1994).

$$IR = [O_3] / [VOC]$$

MIRs are calculated for reference scenarios consisting of a specified meteorological situation, initial pollutant concentrations and emission rates of NO<sub>x</sub> and VOC. If a series of simulations with differing NO<sub>x</sub> initial concentrations and emission rates are made, a scenario will be found in the VOC limited region where the aggregate incremental reactivity reaches a maximum and this is defined as the MIR scenario (Carter, 1994). Once the MIR scenario is known incremental reactivities can be calculated through the simulation of cases with small variations in individual organic compounds.

Ozone formation potentials are highly dependent on the chemical mechanisms for VOC oxidation. To consider reactivity as the basis of a VOC control strategy it is necessary that the calculated MIRs be as accurate as possible. The calculation of accurate MIRs requires that the kinetic oxidation mechanism be based on the best possible science. Because detailed chemical mechanisms, such as Carter's updated chemical mechanism,

have hundreds of parameters, including rate constants, product yields and for photolysis reactions, quantum yields and absorption cross sections, the mechanism was reviewed. Each individual parameter was checked against standard data bases, such as NASA (DeMore et al., 1997), IUPAC (Atkinson et al., 1997; Atkinson, 1994), and the mechanism's overall structure and approach was checked for consistency with the available data. Kinetic parameters that are not well measured in the laboratory must be considered to be highly uncertain and these parameters were identified. High quality of the documentation of the mechanism and its supporting programs is necessary for the credibility of the mechanism and the acceptance of reactivity as a regulatory tool. Therefore the documentation was critically reviewed as well.

In this work Carter's updated base chemical mechanism, the VOCs represented using the assigned mechanistic parameter method, the use of the "lumped molecule" approach and the handling of uncertainty in both the MIR and the regulation were reviewed. The portions of the mechanism that are highly uncertain, due to the lack of laboratory data and where new data may significantly change the calculated MIRs, were documented. Finally the quality of the documentation of the mechanism was assessed.